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THERMAL CONDUCTIVITY AND EUCKEN-TYPE FACTOR FOR THE BINARY MIXTURES H-He, H-Ne, H-Kr and H-Xe

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ABSTRACT. In order to test the recent formulae for the thermal conductivity of polyatomic gas mixtures, the thermal conductivity of H_2–He, H_2–Ne, H_2–Kr and H_2–Xe mixtures have been measured at 30°C and 45°C by using the thick-wire-variant of the hot-wire method. The experimental values of the thermal conductivity of the pure gases and their binary mixtures is lower than those given by Hirschfelder's theory based on the local chemical equilibrium assumption. It has been suggested that this discrepancy between theory and experiments at the temperatures under consideration is due to the non-validity of the condition of local chemical equilibrium. Apart from this drawback Hirschfelder's theory has been found to represent the concentration dependence of the thermal conductivity of polyatomic gas mixtures quite satisfactorily. The more rigorously derived formula of Hirschfelder has been found to represent the thermal conductivity of gas mixtures better than the approximate equation of Mason and Saxena.

I. INTRODUCTION

The problem of heat transfer in multicomponent mixtures of monatomic and polyatomic gases has recently attracted considerable attention. Though Curtiss and Hirschfelder (1949) has obtained expressions for the thermal conductivity of multicomponent mixture of monatomic gases by an extension of the Chapman-Enskog treatment for a binary mixture which is correct to the first approximation, their formula requires too much laborious calculations. In an attempt to overcome this difficulty, Mason (1958), Curtiss and Muckenfuss (1958) and Brokaw (1958) have obtained simpler expressions for the thermal conductivity of multicomponent mixtures of monatomic gases. The difficulty in treating the monatomic gases is only computational but the problem of heat transfer in polyatomic gases and gas mixtures is much more interesting as in this case the exchange of energy between the translational and the internal energies of the molecules need be considered. Eucken (1913) first suggested a correction to the thermal conductivity of polyatomic gases which was based on simple intuitive arguments whose inadequacy was later pointed out by several workers (Chapman and Cowling, 1952; K. Schafer, 1943). Recently, Hirschfelder (1957a) has obtained an expression for the thermal conductivity of a pure polyatomic gas by a formal

treatment in which the molecules in different states of excitation are treated as separate chemical species in local chemical equilibrium. The treatment for a pure polyatomic gas has been extended by Hirschfelder (1957b) to the case of the polyatomic gas mixtures. Mason and Saxena (1958) have made a number of approximations to simplify Hirschfelder's furmula for the mixture conductivities. As accurate data on the thermal conductivity of gas mixtures are not extensive elaborate comparison of the experimental data with the recent theories cannot be made. Recently, Srivastava and his co-workers (1959, 1960a, 1960b) have measured the thermal conductivity of a number of binary mixtures of diatomic and monatomic gases and compared their data with the theory. In order to test further the expression for the thermal conductivity of gas mixtures and also to verify the suggestion of the non-validity of the condition of local chemical equilibrium in the present investigation the paper values of thermal conductivity of H_2-He, H_2-Ne, H_2-Kr and H_2-Xe mixtures at 30°C and 45°C have reported.

2. EXPERIMENT

The apparatus and the procedure adopted for the experiment are similar to those described by Srivastava and Barua (1960) and the constants of the conductivity cell are given in Table I.

TABLE I

Constants of the conductivity cell

	At 30°C	At 45°C
Length of the cell wire ($2l$)	5 9978 cm	5 9987 cm.
Radius of the cell wire (r_1)	0 00500 ,,	0.00500 ,,
Internal diameter of the tube ($2r_2$)	0 3048 ,,	0.3048 ,,
External diameter of the tube ($2r_3$)	0.5915 ,,	0 5915 ,,
Resistance of the cell wire (R_0)	0 83518 Ω	0 88012 Ω
Temperature coefficient of resistance α of the platinum wire	0 00360°C^{-1}	0 00358°C^{-1}
Thermal conductivity λ of the platinum wire in cal. cm^{-1}. sec^{-1}. °C^{-1}	0.167	0 168
Cell constant ($1-C$)	0.9942	0.9941

As shown by Kannuluik and Martin (1934) the solution of the differential equation for heat flow is given by

$$f(\beta l) = \frac{1}{(\beta l)^2}\left(1-\frac{\tanh \beta l}{\beta l}\right) = \frac{2\pi r_1^2 \lambda J(R-R_0)}{R_0 \alpha I^2} \qquad (1)$$

with

$$\beta^2 = \frac{2h}{r_1\lambda} - \frac{I^2R_0\alpha}{2\pi r_1^2\lambda JI}, \quad h = \frac{Ku}{r_1 \ln (r_2/r_1)} \tag{2}$$

where R is the resistance of the wire when a current of I amp. is flowing through it, R_0 is the resistance of the cell wire at the bath temperature for $I = 0$. λ, K_u are the thermal conductivities of the wire and the gas respectively.

In Table II are shown the observations taken for H_2-He mixtures at 30°C which may serve as an example for the observations taken for other mixtures. In the Tables K_u has been calculated from Eq. (1) and (2), K_u' is the value of K_u reduced to the bath temperature and K' is the value of the conductivity when temperature jump and wall effect are corrected for and K is the value obtained after correcting for the asymmetry in the construction of the cell given by the relation $K = K'(1-\delta)$. In Tables III and IV are given the observed values of the thermal conductivity of the mixtures H_2-He, H_2-Ne, H_2-Kr and H_2-Xe at 30°C and 45°C which are plotted in Figs. 1 and 2.

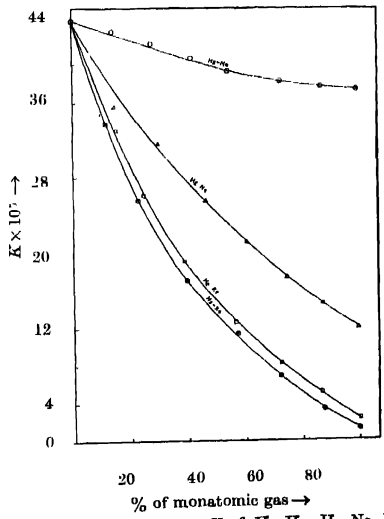

Fig. 1. Thermal conductivity K of H_2-He, H_2-Ne, H_2-Kr and H_2-Xe mixtures of different compositions at 30°C.

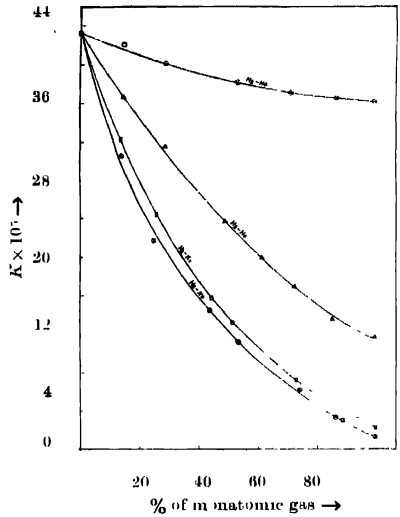

Fig 2. Thermal conductivity K of H_2–He, H_2–Ne, H_2–Kr and H_2–Xe mixtures of different compositions at 45°C

TABLE II

Thermal conductivity K of H_2-He mixtures
cal. $cm^{-1}sec^{-1}.^oC^{-1}$ at 30°C

% of He	I in mA	$R-R_0$ in $m\Omega$	$K_H \times 10^5$	$K_H' \times 10^5$	$K' \times 10^5$	$K \times 10^5$
100	208.42	6 247	36.89	36 79	36 49	36 32
87.13	207 68	6.023	37.24	37.14	36 84	36 63
71.36	209.78	6 040	37.88	37.78	37.39	37.17
53 28	214 62	6 125	39.06	38 95	38 58	38 36
45.62	213 75	6.008	39.59	39.49	39 18	38.95
28.91	212 31	5 690	41 25	41.13	40 75	40 52
14.64	210 16	5.323	43.24	43 12	42.72	42 47
0	213.48	5 289	44.90	44.89	43.49	43.20

TABLE III

Thermal conductivity K of H-He, H-Ne, H-Kr and H-Xe mixtures at 30°C

Gas Mixture	H_2–He		H_2–Ne		H_2–Kr		H_2–Xe	
	% of He	$K \times 10^5$	% of Ne	$K \times 10^5$	% of Kr	$K \times 10^5$	% of Xe	$K \times 10$
	100	36 32	100	11.65	100	2 256	100	1 261
	87.13	36 63	85 61	13.52	88 62	3.011	86.24	3 374
	71.36	37 17	72 83	17 04	73.26	7.254	74 31	6.205
	53 28	38 36	61 31	20 01	51 39	13.31	54.62	11 15
	45 62	38 95	48.93	23 70	44 62	15.82	43.79	14.40
	28.91	40 52	28 93	31 62	25 84	24.30	25 68	21.78
	14 64	42 47	14 82	36 65	13.63	32 27	14 31	30.62
	0	43 20	0	43 16	0	43 91	0	43 16

TABLE IV

Thermal conductivity K of H-He, H-Ne, H-Kr and H-Xe mixtures at 45°C

Gas Mixture	H–He		H–Ne		H–Kr		H–Xe	
	% of He	$K \times 10^5$	% of Ne	$K \times 10^5$	% of Kr	$K \times 10^5$	% of Xe	$K \times 10^5$
	100	37.31	100	12 00	100	2 347	100	1 322
	86.75	37.66	86.71	14 61	85.62	5 074	87 45	3.283
	73 21	38 31	74 86	17 31	72.41	8 208	72 31	6 945
	54 62	39 25	60 41	21.16	56.39	12.57	57 62	11 48
	41 36	70 40	46 54	25 55	38 64	16 04	40 39	17.10
	27.81	42.35	29 83	31.52	24 31	26 06	22 61	25.80
	14.69	44.03	14 62	35.05	15 42	33.01	12.86	33 78
	0	44 75	0	44 84	0	44.79	0	44 77

3. COMPARISON WITH THEORY

The simple Eucken (1913) expression for the thermal conductivity of a pure polyatomic gas may be written as

$$K = \frac{\eta}{M} [f_{trans} C_{V_{trans}} + f_{int} C_{V_{int}}], \qquad \ldots \quad (3)$$

where K is the thermal conductivity, η the viscosity, M the molecular weight, $C_{V_{trans}}$, $C_{V_{int}}$ are the molar specific heats at constant volume corresponding to the translational and the internal degrees of freedom. $f_{trans}=2.5$ and f_{int} indicate the transfer factors for the translational and the internal motions respectively For simplicity Eucken put $f_{int}=1$, so that Eq. (3) becomes

$$K = K_{mon}\,[(4/15)C_V/R+3/5]. \qquad \ldots \quad (4)$$

where K_{mon} is the thermal conductivity of the gas when it is taken to be monatomic. Actually, however, internal energy is transported by a diffusion mechanism (Chapman and Cowling, 1952, Schäfer, 1943) so that $f_{int}=1$ should be replaced by $f_{int}=\rho D/\eta$ (where ρ is the density, D the self-diffusion coefficient and η the viscosity) and Eq. (4) becomes,

$$K = \frac{\eta}{M}\left[\,2.5\,C_{V_{trans}} + (\rho D/\eta)C_{V_{int}}\,\right] \qquad \ldots \quad (5)$$

Hirschfelder (1957a) has obtained the following expression for the thermal conductivity of a pure polyatomic gas by considering the molecules in different states of excitation as separate chemical species which are in local chemical equilibrium,

$$K/K_{mon} = (1-\delta_f)+\delta_f \rho D C_p/C_{pf}. \qquad \ldots \quad (6)$$

where $\delta_f = \rho D C_{pf}/K_{mon}$, $C_{pf}=5R/2$. The values of δ_f has been tabulated for several molecular models and it has been shown that δ_f varies very little with temperature and it is possible to assign to δ_f an average value of 0.885 so that Eq. (6) becomes

$$K/K_{mon} = 0.354 C_V/R+0.469 \qquad \ldots \quad (7)$$

By extending the treatment applied to a pure polyatomic gas Hirschfelder (1957b) has obtained the following expression for the thermal conductivity of a binary mixture of polyatomic gases

$$K_{mix} = K_{mix(mon)}+[K_1-K_{1\ mon}]\,[1+(x_2/x_1)(D_{11}/D_{12})]^{-1} \qquad \ldots \quad (8)$$
$$+[K_2-K_{2mon}]\,[1+(x_1/x_2)(D_{22}/D_{12})]^{-1}$$

where K_1, K_2 are the thermal conductivities, D_{11}, D_{22} are the coefficients of self-diffusion and x_1, x_2 are the molefractions for the components 1 and 2 of the mixture. D_{12} represents the coefficient of inter-diffusion.

In the present case the gas mixture consists of a diatomic gas denoted by the subscript 1 and a monatomic gas denoted by the subscript 2 so that Eq. (8) becomes

$$K_{mix} = K_{mix(mon)}+[K_1-K_{1\ mon}]\,[1+(x_2/x_1)(D_{11}/D_{12}]^{-1} \qquad \ldots \quad (9)$$

The calculation of K_{mix} from Eq. (8) involves laborious computation and the knowledge of force laws between the molecules is necessary which is not easily available. Mason and Saxena (1958) have however tried to simplify Eq. (8) by a number of approximations and their formula may be written as,

$$K_{mix} = \sum_{i=1}^{n} K_i \left[1 + \sum_{\substack{j=1 \\ (i \neq j)}}^{n} G_{ij} \frac{x_j}{x_i} \right]^{-1} \quad \ldots \quad (10)$$

with

$$G_{ij} = \frac{1.065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_j} \right)^{-\frac{1}{2}} \left[1 + \left(\frac{K_i^0}{K_j^0} \right)^{\frac{1}{2}} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2 \quad \ldots \quad (11)$$

where x_i, x_j are the molefractions, M_i, M_j the molecular weights of the components i and j respectively, K_i^0, K_j^0 are the thermal conductivities when the gases are treated as monatomic and are related to the viscosities η_i, η_j by the relation

$$K_i^0/K_j^0 = \frac{\eta_i M_j}{\eta_j M_i} \quad \ldots \quad (12)$$

When η_i and η_j are known experimentally, K_i^0/K_j^0 may be calculated from Eq. (12). In case the experimental viscosity data are not available, specific heat data may be used to obtain K_i^0/K_j^0 In order to compute K_{mix} from Eq. (10) the experimental values of K_i and K_j are to be used

For comparing with the theory K_{1mon} was calculated to the first approximation on the Lennard-Jones (12 : 6) model from the expression

$$K_{1\,mon} = \frac{1989.1\sqrt{T/M}}{\Omega^{(2,2)*}(T^*)\sigma^2} \quad \ldots \quad (13)$$

where $\Omega^{(2,2)*}(T^*)$ is a collision integral which has been tabulated (Hirschfelder, Curtiss and Bird, 1954) as a function of $T^* = kT/\epsilon$, σ and ϵ/k being the potential parameters in Å and °K respectively. When K_{mon} is known, the experimental value of the Eucken factor K_{exp}/K_{mon} can be calculated In order to calculate K/K_{mon} from Hirschfelder's Eq (6), δ_f was taken from the tables (Hirschfelder 1957a) and specific heat data were obtained from the recent Tables published by the National Bureau of Standards (1955). By knowing K_{exp}/K_{mon}, the experimental value of δ_f may be calculated from Eq.(6) and the corresponding value of f_{int} from the relation $f_{int} = 3/2\delta_f$. Similar calculations were done for the data obtained by other workers. The results of these calculations are indicated in Table V.

In order to calculate K_{mix} from Eq. (9), $K_{mix(mon)}$, D_{11}, D_{12} were calculated on the Lennard-Jones (12 : 6) model from the expressions obtained on the Chapman-Enskog theory (Hirschfelder, Curtiss and Bird, 1954). The force constants were taken as those determined from viscosity data except in the case of Kr for

which the force constants determined by Saxena (1957) from thermal conductivity data were used. The results of these calculations are given in Tables VI- XIII.

TABLE V

Eucken factor and f_{int} for H_2

T°K	K_{exp} given by	Eucken factor K_{exp}/K_{mon}	Eucken factor K/K_{mon} from Eq.(6)	Eucken factor K/K_{mon} from Eq.(4)	$f_{int} = \frac{4}{5}\delta f$ From expt	$f_{int} = \frac{4}{5}\delta f$ From Table
303.2	Present Work	1.312	1.343	1.259	1.121	1.330
318.2	-do	1.314	1.348	1.261	1.162	1.331
273.2	Keyes (1952)	1.289	1.326	1.251	1.155	1.328
300.2	Johnston & Grilly (1946)	1.286	1.345	1.259	1.103	1.330
320.2		1.288	1.348	1.262	1.112	1.331
311.2	Srivastava & Srivastava (1959)	1.296	1.344	1.259	1.142	1.331

In column 3, K_H is the value of K_{mix} calculated from Eq. (9) with the theoretical value of δ_f and K'_H in column 4 are those obtained with the experimental value of δ_f. For calculating K_{mix} from Eq (10), viscosity data were used for H_2-He, and H_2-Ne and specific heat data for H_2-Kr and H_2-Xe These calculated values are indicated as K_{MS} in column 5 of Tables VI-XIII Columns 6 and 7 give the values of the Eucken-type factors for the mixtures $K_{exp}/K_{mix(mon)}$ and $K'_H/K_{mix(mon)}$ The experimental values of K_{mix} were read from suitable interpolation graphs.

An interesting test of the algebraic form of Hirschfelder formula for the gas mixture may be made in the following way :

Eq.(9) may be written as

$$K_{mix} - K_{mix(mon)} = \frac{K_1 - K_{1\,mon}}{+(x_2/x_1)(D_{11}/D_{12})} \qquad (14)$$

or $y = mx + C$

where $y = 1/(K_{mix} - K_{mix(mon)})$; $x = x_2/x_1$; $m = (D_{11}/D_{12})/(K_1 - K_{1\,mon})$;

$$C = 1/K_1 - (K_{1\,mon})$$

so that a plot of y vs x should be a straight line. The $y-x$ values for the different gas mixtures have been given in columns 8 and 9 of the Tables VI--XIII and

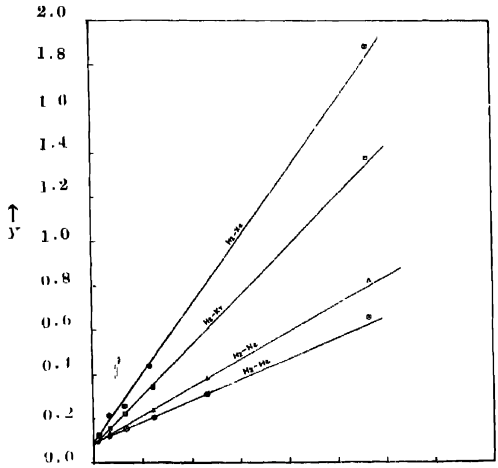

Fig. 3. x–y graphs for H_2–He, H_2–Ne, H_2–Kr and H_2–Xe at 30°C.

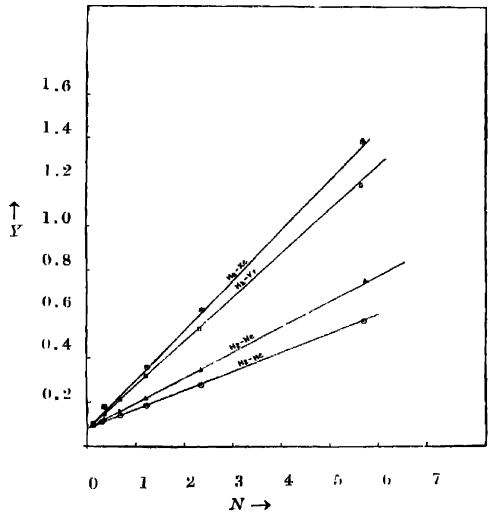

Fig. 4. x–y graphs for H_2–He, H_2–Ne, H_2–Kr and H_2–Xe at 45°C.

are plotted in Figs. 3 and 4. The intercept on the y-axis gives the value of K_1 and the slope gives the value of D_{11}/D_{12} from which D_{12} can be obtained by knowing D_{11}.

TABLE VI

Thermal conductivity and Eucken-type factor for H_2-He mixture at 30°C

% of He	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq.(9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from Eq.(10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
100	36.32	36.32	36.32	36 32	1 000	1.000		
85	36 80	37.12	37 06	37 01	1 038	1.046	0 719	5 666
70	37.44	37.58	37 45	37 86	1 096	1 096	0 306	2 333
55	38 29	38 55	38 36	38.88	1 145	1 148	0 206	1 223
40	39 45	39 80	39 55	40.05	1 195	1 199	0 155	0 667
25	40 96	41 37	41 06	41 39	1.246	1 249	0 123	0 333
10	42 73	43 25	42 88	42 88	1.293	1 298	1 103	0 111
0	43 30	44 42	43.20	43 20	1 312	1 312		

TABLE VII

Thermal conductivity and Eucken-type factor for H_2-He mixture at 45°C

% of He	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq (9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from Eq.(10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
100	37 31	37 31	37.31	37 31	1 000	1.000		
85	37 92	38 07	37.95	38.13	1 045	1.046	0.599	5 667
70	38 60	38.73	38.47	30.11	1 105	1 101	0.275	2 333
55	39.55	39.77	39.62	40.25	1 157	1.160	0.186	1.223
40	40 88	41 12	40 82	41.56	1 212	1 210	0 140	0.667
25	42.57	42.79	42 47	43.03	1 264	1 261	0 113	0.333
10	44 46	44 89	44.56	44 57	1 304	1 307	0 097	0 111
0	44.75	46 03	44 75	44.75	1 314	1 314		

TABLE VIII

Thermal conductivity and Eucken-type factor for H_2-Ne mixture at 30°C

% of No	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq.(9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from Eq.(10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
100	11.65	11 65	11.65	11 65	1.000	1 000	.	.
85	14 25	14.25	14.23	15.52	1.081	1.080	0 822	5 667
70	17 74	17 97	17 83	20.07	1.174	1.180	0 380	2 333
55	21.80	22.01	21 80	24.69	1.240	1.240	0 237	1 223
40	26 58	26.78	26 49	28.68	1.287	1 282	0 169	0 667
25	32.24	32.47	32.09	34 71	1.315	1.309	0 129	0 333
10	38.88	39 18	38.71	40 02	1 319	1.316	0 104	0 111
0	43 16	44 42	43.16	43 16	1.311	1.311	. .	.

TABLE IX

Thermal conductivity and Eucken-type factor for H_2-Ne mixture at 45°C

% of No	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq (9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from (Eq.10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
100	12 00	12 00	12 00	12 00	1.000	1 000	. .	...
85	14 94	15 06	15.00	16.10	1 098	1 102	0 752	5.667
70	18.59	18 68	18 57	20.91	1 185	1 183	0.345	2.333
55	22 71	22.87	22.69	25 81	1.246	1 245	0.223	1.223
40	27.81	28 00	27 74	30 03	1 292	1 289	0 159	0.667
25	33.52	33 72	33 39	36 43	1 321	1 316	0.123	0.333
10	40 56	40.68	40.37	42 09	1.340	1.334	0.0971	0.111
0	44.84	46 03	44 84	44 84	1.317	1.317	....	....

TABLE X

Thermal conductivity and Eucken-type factor for H_2-Kr mixture at 30°C

% of Kr	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq.(9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from Eq (10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
100	2 256	2 256	2 256	2.265	1 000	1 000	.	.
85	4 602	4 903	4.876	5 324	1.168	1 216	1 390	5 667
70	9 016	8 299	8.240	8 901	1 264	1 299	0.597	2 333
55	12 20	12.53	12.43	13 36	1 311	1 336	0 345	1.223
40	17 62	17 95	17 80	18 96	1 343	1 338	0 224	0 667
25	24 84	25 13	24 72	26 18	1 345	1 344	0 155	0 333
10	35.02	35 25	34 97	35 75	1.346	1 344	0 111	0 111
0	43 21	44 42	43 88	43 21	1.312	1 312	.	. . .

TABLE XI

Thermal conductivity and Eucken-type factor for H_2-Kr mixture at 45°C

% of Kr	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq (9)	$K'_H \times 10^5$ from Eq (9)	$K_{MS} \times 10^5$ from Eq (10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	y	x
00	2 347	2.347	2 347	2 347	1 000	1 000	.	.
85	5 160	5 281	5 246	5 510	1 195	1 214	1.491	5 667
70	8 600	8.775	8 695	9 310	1 280	1 294	0 531	2 333
55	12 86	13 15	13.01	13.99	1 317	1 334	0 322	1.223
40	18 31	18.74	18.54	19.83	1.350	1 352	0 217	0 667
25	25 66	26.04	25 76	27 35	1 351	1 358	0 156	0 333
10	36 46	37 60	36 59	37 32	1 355	1 359	0 105	0 111
0	44.79	46 03	44.79	44.79	1 315	1 315	.	. .

TABLE XII

Thermal conductivity and Eucken-type factor for H_2-Xe mixture at 30°C

% of Xe	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq (9)	$K'_H \times 10^5$ from Eq.(9)	$K_{MS} \times 10^5$ from Eq.(10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	η	ϵ
100	1 261	1 261	1 261	1 261	1 000	1 000		
85	3.745	3.807	1.779	3.722	1 176	1 231	1.898	5 667
70	6 812	6 864	6 803	6 787	1 318	1 316	0 814	2 333
55	10.61	10.77	10 67	10 71	1.340	1 347	0 398	1 223
40	15.81	16.14	15.99	15.91	1.338	1 353	0 253	0 667
25	21.68	21 92	21 74	23.85	1 283	1 287	0 211	0.333
10	33 49	33 79	33 74	34 22	1 347	1 346	0 155	0 111
0	43 16	44 42	43.16	43 16	1 311	1.311		

TABLE XIII

Thermal conductivity and Eucken-type factor for H_2-Xe mixture at 45°C

% of Xe	$K_{exp} \times 10^5$	$K_H \times 10^5$ from Eq.(9)	$K'_H \times 10^5$ from Eq (9)	$K_{MS} \times 10^5$ from Eq.(10)	$\frac{K_{exp}}{K_{mix(mon)}}$	$\frac{K'_H}{K_{mix(mon)}}$	η	ϵ
100	1.322	1 322	1 322	1 322	1.000	1 000		
85	3 936	3 988	3 931	3 916	1 245	1 243	1 293	5.667
70	7 062	7 191	7 066	7 142	1 315	1.316	0 590	2 333
55	11 05	11 27	11 06	11 26	1 345	1 346	0 353	1 223
40	16 31	16 71	16 40	17 61	1 348	1 355	0 238	0.667
25	23 58	24 13	23 68	24 24	1 349	1.355	0 164	0 333
10	34 35	35 12	34 48	35 25	1 336	1 342	0 116	0 111
0	44.77	46 03	44 77	44 77	1 315	1 315		

The values of K_1 and D_{12} obtained from the graphs have been recorded in Table XIV together with the value of $K_{1\ exp}$ and the values of D_{12} calculated on the Lenard-Jones (12 : 6) model.

TABLE XIV

Thermal conductivity and inter-diffusion coefficients from graphs

T°K	Gas Mixture	$K_1 \times 10^5$		D_{12}	
		from graph	from expt.	from graph	calculated on the L–J (12:6) model
303 2	H_2–He	43 79	43 20	1.332	1.592
	H_2–Ne	43.65		1.143	1 152
	H_2–Kr	43 45		0.654	0 724
	H_2–Xe	42.87		0 021	0 618
318 2	H_2–He	44 99	44 75	1.620	1 729
	H_2–Ne	45 24		1 184	1 193
	H_2–Kr	45 32		0.678	0 785
	H_2 Xe	44.98		0.659	0 672

DISCUSSION OF RESULTS

For pure H_2, it may be seen from Table V, that all the experimental measurements of the thermal conductivity is consistently less than those given by Hirsfelder's Eq. (6) based on local chemical equilibrium assumption and so the experimental values of f_{int} are also less than the limiting value of ~ 1.3 This discrepancy between theory and experiments as has already been suggested (Srivastava and Barua, 1960) may be due to comparatively slow rate of rotational-translational transfer of energy. It is also to be noted that Waelbroeck and Zucker-brodt (1958) have also reached the same conclusion from their measurements on the thermal conductivity of O_2 and H_2 down to very low pressures Actual measurements (e.g Stewart and Stewart, 1948) show that for H_2 about 1 collision out of 300 brings about a rotational translational transfer of energy whereas practically every collision brings about a translational-translational transfer On the other hand Eucken's derivation (i.e. $f_{int} = 1$) is based on the assumption that the rotational-translational transfer rate is negligible. The actual cases are in between the conditions imposed upon by Hirschfelder's and Eucken's derivations. Hence it is to be expected that f_{int} should lie between 1 and 1 3 which is actually found to be so.

In Tables VI—XIII it can be seen that the calculated values of K_{mix} from Hirschfelder's Eq.(9) are always higher than the experimental values At least a part of this disagreement must be due to the higher value of the thermal conductivity of pure H_2 given by the Hirschfelder's theory. When this is corrected for by taking the experimental value of K_1 in calculating K_{mix}, it is seen that the agreement between the experimental and the calculated values of the mixture

conductivities becomes excellent This points to the conclusion that Hirschfelder's Eq.(9) is capable of predicting correctly the concentration dependence of the mixture conductivities. A further support to this conclusion is given by the nearly straight line character of the x --y graphs for the various mixtures (Figs. 3 and 4). The approximate formula of Mason and Saxena (1958) Eq (10) is found to represent the experimental data much worse than the more rigorous formula of Hirschfelder which is apparently due to the number of approximations made in the derivation of Eq. (10)

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